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(54) Method for preparing a catalyst for the synthesis of 1,2-dichloroethane.

(57) A method for preparing a catalyst for the synthesis of 1,2-dichloroethane by oxychlorination of C_2H_4 within a fluidized bed, said catalyst containing magnesium, from 1 to 10% by weight of Cu and a carrier consisting of Al_2O_3 , said carrier being impregnated, with an aqueous solution containing both $CuCl_2$ and $MgCl_2$, the amount of $MgCl_2$ being such that the molar ratio:

$$X = \frac{\text{Al on the surface}}{\text{Cu on the surface}}$$

as defined in the text, is at least 40% higher than the molar ratio:

$$Y = \frac{\text{Total Al present within the catalyst}}{\text{Total Cu present within the catalyst}}$$

the ratio $W = X:Y$ being therefore ≥ 1.40 and the surface area of the carrier being comprised between 80 and 170 $m^2.g.$

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METHOD FOR PREPARING A CATALYST FOR THE SYNTHESIS
OF 1,2-DICHLOROETHANE

This invention relates to a method for preparing a catalyst for
5 the synthesis of 1,2-dichloroethane by oxychlorination of C_2H_4 within a
fluidized bed, said catalyst containing from 1 to 10% by weight of Cu
and furthermore Mg, as well as a carrier consisting of Al_2O_3 .

BACKGROUND OF THE INVENTION

Field of the invention

10 Catalysts of the aforesaid type have been described, as well as
the respective methods of preparing them, in several patents. See, for
instance, British patent 971 996, USP 4 125 534, British patent 1 345 653
and the US pending application of Enrico Cavaterra et al Serial
No. 591 993, filed March 21, 1985 which disclose the impregnation of
15 alumina with solutions of $CuCl_2$ and $MgCl_2$.

In the first cases, however, no precise enough direction is given
to obtain the high yields required by modern plants and, at the same
time, a satisfactory degree of fluidization.

These results, on the other hand, can be obtained by using the
20 catalyst according to the aforesaid Cavaterra et al application. Howev-
er, in this case, there are also drawbacks; in fact, said application
teaches that excellent performances can be achieved only if the catalyst
is treated with hydrochloric acid (HCl), which may involve problems
concerning ecology and corrosion in the plant, during the catalyst
25 preparation.

Description of the prior art

It has now been surprisingly found that the same excellent perfor-
mances as those achieved according to the Cavaterra et al application
can be achieved without using HCl during preparation of the catalyst,
30 provided $CuCl_2$ and $MgCl_2$ are added at the same time and provided the
surface area of the carrier is comprised between 80 and 170 m^2/g . In

other words, it has been observed that, when the surface area of the carrier has a value comprised within said given range, (and provided the amount of magnesium chloride is sufficiently high), the magnesium chloride acts as regulator of the copper on the surface, a function
 5 which had previously been ascribed to HCl.

In broad terms, the molar ratio Mg/Cu in the impregnating solution must be comprised between 0.4 and 1.2 and in any case be such that the molar ratio:

$$10 \quad X = \frac{\text{Al on the surface}}{\text{Cu on the surface}}$$

as defined hereinafter, is at least 40% higher than the molar ratio:

$$Y = \frac{\text{total Al present within the catalyst}}{\text{total Cu present within the catalyst}}$$

namely: $W = X/Y \geq 1.40$.

- 15 According to a preferred embodiment of the invention:
- the catalyst contains from 3 to 6% by weight of copper;
 - said X ratio is equal to or higher than 40:1;
 - the amount of magnesium in the catalyst (and in the solution) is comprised between 0.5 and 1.1 moles per mole of copper.

20 Said molar ratio:

$$X = \frac{\text{Al on the surface}}{\text{Cu on the surface}}$$

must be determined according to the technique known as XPS analysis (described hereinafter), that supplies the data pertinent to a superficial micro-layer having a thickness comprised between 2 and 3 nm
 25 (20-30 Ångstrom). Generally, according to the method of the invention, the copper concentration on the surface has to be zero or, in any event, much lower than the copper concentration within the layers directly underlying the superficial layer, said superficial layer having substantially a thickness from 2 to 3 nm.
 30

The catalysts according to the invention display excellent fluidization features and maintain high HCl conversions, as well as in the case of high HCl/C₂H₄ ratios, so that high dichloroethane (DCE) yields with respect to C₂H₄ are achieved.

35 In the catalysts according to the invention, considering the single granule, the Cu lies prevailing inside the pores, i.e. it is laid on the inner surface of same; such proportion of Cu, although when involved in the conversion cycles and in the equilibria among the

various forms (Cu_2Cl_2 , Cu_2Cl_4 , etc.), depending on the $\text{HCl}/\text{C}_2\text{H}_4$ feed ratio, it does not give place to the sticking phenomenon, that, on the contrary, affects the zones of possible contact among the different granules.

5 The outstanding feature of the present catalysts is that, in practice, the active part is almost completely segregated inside the pores of the carrier, the Cu concentration on the outer surface being very slight and in any event clearly lower than the Cu concentration on the outer surface which is a disadvantage of the conventional catalysts,
10 as shown by measurements carried out by means of the XPS technique. Furthermore, it remains the same after long periods of time.

By using these catalysts, the reaction within a fluidized bed can be carried out without any adverse effect on the fluidization, using high $\text{HCl}/\text{C}_2\text{H}_4$ ratios in the feed and with high HCl conversions, so that
15 high yields of DCE are obtained with respect to ethylene. The conditions of use of these catalysts do not substantially differ from those of the catalysts previously described in the art. C_2H_4 , HCl and a gas containing O_2 (generally air) are fed into a gaseous phase, pre-heated to a temperature close to, but not higher than, the reaction temperature, the
20 latter comprised between 200 and 250°C, preferably between 220 and 235°C. The other operating parameters are generally comprised within the following ranges:

- (A) Air/ethylene ratio: it must be such that the O_2 content, in the gaseous exhausts, after condensation of DCE, H_2O and HCl, is
25 comprised between 3 and 10% by volume.
- (B) HCl/ethylene ratio: it must as close as possible to the stoichiometric value (2/1 molar) compatible with the maintenance of good fluidization conditions of the catalytic bed and of a sufficiently high conversion of HCl, conditions which depend, as already noted,
30 on the specific catalyst.
- (C) Contact time (expressed as a ratio of the volume of the catalytic bed in a fluidized state to the volumetric flow of the reactant mixture, under the temperature and pressure conditions existing in the catalytic bed); it depends essentially on the specific type of catalyst utilized; generally it ranges between 10 and 40 seconds,
35 preferably between 20 and 30 seconds.
- (D) Linear velocity of the gases (expressed in cm/s): it is chosen within the range between the rate of a minimum fluidization and

the carrying along rate, both being typical for the type of catalyst; generally, said rate is comprised between 10 and 50 cm/s, and preferably between 20 and 40 cm/s.

- 5 (E) Total pressure during the reaction (important for achieving an effective contact among the reactants, in a gaseous phase, and the catalyst, in a solid phase): generally, pressures used are higher than atmospheric pressure, up to 6 bars; at higher pressures energy waste becomes predominant, due to the compression work.

The following examples are given by way of non-limitative illustration.
10

OPERATING CONDITIONS COMMON TO THE DIFFERENT EXAMPLES

Measurement of the outer surface concentration of Cu was carried out by means of the XPS technique (see C.D. Wagner: Handbook of X-Ray Photoemission Spectroscopy; Perkin Elmer Co., Eden Prairie; 1979) based
15 on X-ray irradiation and on the measurement of the energy level and of the energy intensity of the electrons emitted by the solid. The energy level of such electrons is characteristic of the element and the energy intensity is proportional to the number of atoms present in the volume of sample, down to a depth substantially of 2 to 3 nm (20-30 Å) from the
20 surface. As the average size of the catalysts is about 50 micrometers (in literature values from 20 to 80 nm are usually cited), the measurement value of the atomic concentrations refers to about 1 ten-thousandth of the granule diameter, namely, essentially to its outer surface. In detail, a small amount of a sample (a few milligrams) was pressed onto a
25 small plate of pure indium in order to obtain an analyzable surface having an area equal to several square nanometers; the samples were then analyzed under a high-pushed vacuum at a basic pressure of $2 \cdot 10^{-7}$ Pa, using an X-ray source working at 400 W and fitted with a Mg anode ($K\alpha$ radiation of magnesium). The photoemission spectra of the present
30 elements, i.e. O/1s, Cl/2p, Mg/2p, Al/2p, were gathered under conditions of high resolution by using a computer for the digitalized acquisition of the data, with a maximization of the signal/noise ratio. After removal of the background noise, the areas of the photoemission peaks were calculated by means of numerical integration; the intensity value thus
35 obtained, corrected for the respective sensitivity factor, was directly proportional to the surface atomic concentration of the respective element.

All catalysts were prepared by means of the "dry impregnation" technique, described for instance by A.V. Neimark, L.I. Kheifez and V.B. Fenelonov on Ind. Eng. Chem. Prod. Res. Dev. 1981, 20, page 441.

EXAMPLE 1 - Preparation of the Catalyst by means of a "dry impregnation"

5 A microspheroidal alumina having a surface area of 170 sq.m/g and an average particle diameter of 50 nm was chosen as carrier and the volume of the impregnating solution was equal to the volume of the alumina pores. Said solution contained:

- 10 - CuCl_2 , in an amount such that the final catalyst contained 4.16% by weight of Cu;
- 0.736 moles of MgCl_2 per mole of Cu.

In further detail, the operating conditions described were as described hereinafter:

15 (A) 10.5 l of deionized water were heated to 80°C and 6.083 kg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; 5,291 kg of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were then added, under stirring.

Heating and stirring were continued until a complete dissolution was achieved and the solution thus obtained was then cooled to 25°C;

20 (B) 43.0 kg of said alumina were put into a rotary container and the solution obtained according to (A) was slowly sprayed, over a period of 1 hour, onto the alumina, kept under stirring by the rotation of the container, taking care to avoid the formation of clots. Afterwards, the temperature was raised to 150°C, with a
25 gradient of 25°C/h and said temperature was kept at 150°C for a further 3 hours. The catalyst was then slowly cooled to 40°C, keeping the container under constant rotation. The analysis gave the results shown in Table 1.

EXAMPLES 2, 3, 4 (Behavior of the Catalyst)

30 The catalyst of Example 1 was introduced into a glass reactor having a diameter of 4 cm and a height of 3 m, capable of withstanding pressures up to 6 bars. Said catalyst was then activated in situ at 180°C for 4 hours in the air. The thus activated catalyst was tested in an oxychlorination of C_2H_4 within a fluidized bed at a pressure of
35 4 bars (absolute), according to an air/ C_2H_4 molar ratio equal to 3.2 and with a contact time of 28 seconds; data and results obtained are shown in Table 2.

EXAMPLE 5 (Comparative)

Example 1 was repeated but without any addition of Mg; the results obtained are shown in Table 1.

EXAMPLES 6 AND 7 (Comparative)

- 5 Examples 2 and 3 were repeated, but the catalyst was replaced by the product lacking in magnesium, prepared according to Example 5. Data and results obtained are shown in Table 2. All these examples show that the lower concentrations of Cu on the surface (corresponding to higher Al/Cu ratios) lead to better fluidization characteristics of the cata-
 10 lyst, which allows to work with higher $\text{HCl}/\text{C}_2\text{H}_4$ feed ratios and thus to obtain higher yields in dichloroethane.

TABLE 1

Examples	% of atoms on the surface			$X = \frac{\text{Al on the surface}}{\text{Cu on the surface}}$	$Y = \frac{\text{Total Al}}{\text{Total Cu}}$	$W = \frac{X}{Y}$
	Cu	Cl	Al			
1	2.1	7.7	90.2	42.9	25.3	1.69
5 (*)	3.7	7.7	88.6	24.1	26.7	0.90

(*) Comparative.

TABLE 2

Exam- ple	$\frac{\text{Al}}{\text{Cu}}$	Activation T (°C)	Oxychlori- nation T (°C)	$\text{HCl}/\text{C}_2\text{H}_4$ (by moles)	DCE yield (molar % on fed C_2H_4)	HCl Conversion (%)	Fluidization
2	42	180	225	1.824	91.1	99.9	Excellent
3	42	180	225	1.946	96.6	99.3	Excellent
4	42	180	225	1.990	97.7	98.2	Excellent
6	24.1	180	225	1.816	90.7	99.9	Good
7	24.1	180	225	1.926	95.7	99.4	Bad

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C L A I M S

- 1.- A method for preparing a catalyst for the synthesis of 1,2-dichloroethane by oxychlorination of C_2H_4 within a fluidized bed, said catalyst containing from 1 to 10% by weight of Cu, magnesium and a carrier consisting of Al_2O_3 , said method being characterized in that the carrier is impregnated with an aqueous solution containing both $CuCl_2$ and $MgCl_2$, the amount of $MgCl_2$ being such that the molar ratio:

$$X = \frac{Al \text{ on the surface}}{Cu \text{ on the surface}}$$

- as defined in the text, is at least 40% higher than the molar ratio:

$$Y = \frac{\text{Total Al present within the catalyst}}{\text{Total Cu present within the catalyst}}$$

the ratio $W = X:Y$ being therefore, ≥ 1.40 and the surface area of the carrier being comprised between 80 and 170 m^2/g .

- 2.- The method of claim 1, wherein said catalyst contains from 3 to 6% by weight of Cu.

3.- The method of claim 1, wherein the ratio X is equal to or higher than 40.

- 4.- The method of claim 1, wherein the amount of magnesium in the catalyst is comprised inclusively between 0.4 and 1.2 moles per mole of copper.

- 5.- The method of claim 1, wherein the copper concentration on the outer surface of the carrier is zero or at least much lower than the copper concentration in the layers directly underlying the superficial layer, said superficial layer having substantially a thickness from 2 to 3 nm.

6.- The method of claim 1, wherein the amount of magnesium in the catalyst is comprised inclusively between from 0.5 and 1.1 moles per mole of copper.

- 7.- The method of claim 1, wherein the dry impregnation technique is adopted for the impregnation of the carrier with said solution.